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Differential study of substituted and unsubstituted cobalt phthalocyanines for gas sensor applications

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ABSTRACT

The conductivity of CoPc (cobalt phthalocyanine) and Co[$(SO_3Na)_{2,3}$Pc] was measured under a flow of two different gases (NH_3 and O_3), during exposure/recovery cycles. It appears that the relative responses are linearly related to the concentration, in the 20–200 ppb range for O_3 and in the 20–200 ppm range for NH_3. Observed during time, the sensing parameters allow a qualitative understanding of the kinetics. The comparative study of those products under both different gases gave interesting results for sensor applications. Whereas CoPc is sensitive to both gases, its sulfonated counterpart is only sensitive to NH_3.

1. Introduction

Molecular materials have been studied since many years [1–3], but their interest highly increased with the development of organic electronics [4,5]. Molecular semiconductors have led to a new field of electronics with components like organic light emitting diodes (OLED) [6] used for TV and computer's screens, organic photovoltaic cells for the energy production [6,7] or organic field-effect transistors (OFET) [8,9] for organic plastic displays [10]. Among molecular semiconductors, phthalocyanines received a particular attention. Their broad physicochemical properties, namely their high thermal and chemical stabilities compared with other organic materials and a rich substitution chemistry, lead to a large flexibility in tuning molecular structures, and therefore in their macroscopic properties [11]. Another application field for molecular semiconductors is that of chemical sensors [12]. Redox active species can modify the density of charge carriers, then the conductivity of sensing materials [13,14]. Additionally, the adsorption of chemical species, and their diffusion, can affect the transport properties of molecular materials, due to a modification of their dielectric constant or by trapping charge carriers. Thus, the sensitivity of molecular semiconductors is usually higher towards strong oxidizing- or reducing-species, in the ppb range for ozone (O_3) and nitrogen dioxide, whereas sensitivities to volatile organic compounds (VOC) are rather in the ppm or in the percent range [15]. It is the reason why ozone, currently present in the 10–20 ppb range inside buildings, can highly disrupt the electrical properties of molecular materials [16,17]. Thus, gases that induce doping or trapping effects on molecular materials can allow a conductimetric transduction process for their detection. Various conductimetric transducers were developed like resistors, organic field effect transistors (OFET) [18–20] and new components like organic diodes [21] and molecular semiconductor-doped insulator heterojunctions (MSDI) [22,23].

A strong interest in gas sensors is related to air quality control. Among pollutants, ozone needs to be detected in the ppb range due to its highly oxidizing power, whereas ammonia (NH_3) needs to be measured in the 10–100 ppm range when detected in industrial wastes control [15].

Among metalated phthalocyanines, cobalt phthalocyanine occupies a particular place due to its use as activated charcoal supported catalytic material for the elimination of sulfur-containing species in kerosene or other oil products [24]. They are also well-studied product in gas sensing realms [25,26]. However, comparative study with the same central metal and different substitutes are minority [25].

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The topic of this article is a comparative study of a pure cobalt phthalocyanine (CoPc) and a substituted product, namely a mixture of sulfonated cobalt-phthalocyanines (s-CoPc), with a mean substitution degree equal to 2.3, supplied by Europhtal company. The choice of those products was made to study the sulfonated substituents effect on the sensing properties and to benefit from different deposition techniques. CoPc is deposited by vacuum evaporation (VE), a clean method that needs a secondary vacuum set-up, whereas s-CoPc can be deposited by solvent cast (SC) due to its solubility in water. This last method is cheaper, an important point for industrial applications.

The withdrawing effect of sulfonated substituents is know to induce a slight shift of the redox potentials of the phthalocyanine derivative compared to its unsubstituted analogue as depicted by J. Zagal et al. for tetrasulfonated phthalocyanine [27]. However, the key difference between both materials remains the hydrophilic character of s-CoPc.

For this study, the transducer was a resistor. Its functional principle was the conductivity variation of a sensing material. A gas adsorbed on the surface induces a doping of the molecular material. The gaseous molecules behave as electron donor or acceptor materials. Thus the conductivity of p-type material increases with acceptor gases and decreases with donor species.

We will discuss the structure of materials and the effect of the polarization method of materials during experiment on their electrical characteristics. Our two kinds of sensors were compared under O_3 and NH_3 as well.

2. Experimental

2.1. Electrodes

The resistors are constituted of a molecular material deposited on the surface of interdigitated electrodes (IDE). IDEs made of indium tin oxide (ITO) are composed of ten pairs of digits deposited on glass substrate with the following dimensions: 125 μm electrode width, 75 μm spacing, 5850 μm overlapping length and 20 nm electrode thickness. Before any material deposition, IDEs on glass were clean with the following protocol. The IDEs were washed in dichloromethane, then ethanol during 30 s with sonic wave and finally dried in air.

2.2. Material deposition

CoPc was deposited onto IDEs by means of classical thermal evaporation (using a VEECO 770 system) at ca. 10^{-6} mbar, and a $2\,\text{Å}\,s^{-1}$ rate. The thickness (100 nm) was controlled by a quartz micro-balance. This method, called vacuum evaporation (VE) has been well studied in literature and polycrystalline films are obtained [28,29].

s-CoPc is an industrial product, a mixture of n-sulfonated CoPc (s-CoPc) know as $Co[(SO_3Na)_{2,3}Pc]$ supplied by the Europthal company as additive 8020. This product was chosen for its solubility in water, something not possible with CoPc. The mother solution was diluted to a concentration of $4.4 \times 10^{-4}\,mol\,L^{-1}$ and deposited directly on the surface of the IDEs with a micro syringe. The component was heated in a desiccator during 1 h at 60 °C and then annealed at 100 °C during at least 15 h, leading to ca. 100 nm-thick films. Connectors were clipped on the IDEs and sticked on with silver paint.

2.3. Gas sensing

All the measurements were carried out in a cylindrical Teflon sensor chamber (ca. $10\,cm^3$ as internal volume). A multimeter Keithley K6517 with incorporated voltage supply was used to measure the current through the sensor. This set-up was controlled by a computer, which saves data of the experiment. However, gas sources feeding the cell were completely different from each other: an analyzer/generator for ozone and gases cylinders for ammonia. So, even for the same measurement, two different workbenches were needed (see Section 2.4).

In order to counter the effect of a possible ionic conduction, alternative positive and negative polarizations were applied as described in Section 3. The samples were biased for 1 s positively and the current was measured before the switching to a negative value, also maintained for 1 s.

The response to the target gases was determined after alternation of exposure and recovery periods. The exposure and recovery times were fixed at 1 and 4 min, respectively. At each gas switching the current was measured. The relative response was calculated by the formula (1).

$$\frac{\Delta I}{I_0} = \frac{I_f - I_0}{I_0} \tag{1}$$

where I_0 is the current value at the beginning of a exposure/recovery cycle and I_f the current value at the end of the same cycle.

This relative variation gives the trend of sensors during a time period. A positive variation means that the $I(t)$ curve increases and reciprocally, a negative variation means that the $I(t)$ curve decreases. This formula corresponds to the maximal variation of the current during a cycle since the current is strictly increasing or decreasing over one period. With this tool, effects of concentration on different molecular materials were studied.

For gas sensing, the conductivity of materials was followed by current measurement. But in order to compare the results with literature, we preferred to use the conductivity to plot the sensor response. The formula (2) allows to convert the current into conductivity.

$$\sigma = \frac{I \times l}{US(2n-1)} \tag{2}$$

where I was dc current through the sensor, l was the distance between two fingers of the sensor, U was the applied bias, S was the surface's section of the IDE and n the number of fingers per electrode.

2.4. The gas workbenches

All experiments were carried out at a working temperature in the range 18–22 °C.

Ozone was generated by an analyzer/generator ($O_3$41 M Environment S.A.), which allows a controlled supply of ozone in air at the ppb level (total mass flow: $1.6\,L\,min^{-1}$). Ozone was generated by UV radiation from the ambient air after filtration on charcoal (removal of NO, NO_2, SO_2, O_3) and silica gel (removal moisture) [30]. The cycles were controlled by a timer that commutes the opening and closing of two electro-valves (see EV1 & EV2 on Fig. 1). The important point is to remember the nature of the two periods: (i) a dynamic exposure under a flow of ozone and (ii) a static recovery. The later avoids the diffusion of humidity from the outlet and ensures that air remains dry during static period, the gas output being linked to a silica gel-containing wash bottle.

For ammonia, a cylinder of a NH_3/Ar mixture containing 1000 ppm of NH_3 was used as a source and an Ar cylinder was used as a diluting gas source. The maximum water contents in ammonia and argon cylinders purchased near Air Liquid are 100 ppm and 2 ppm, respectively. In any case, it corresponds to a very low relative humidity. The flow ($0.5\,L\,min^{-1}$), cycles and gas concentrations were controlled by two mass flow meters (Fig. 2) via a computer. For